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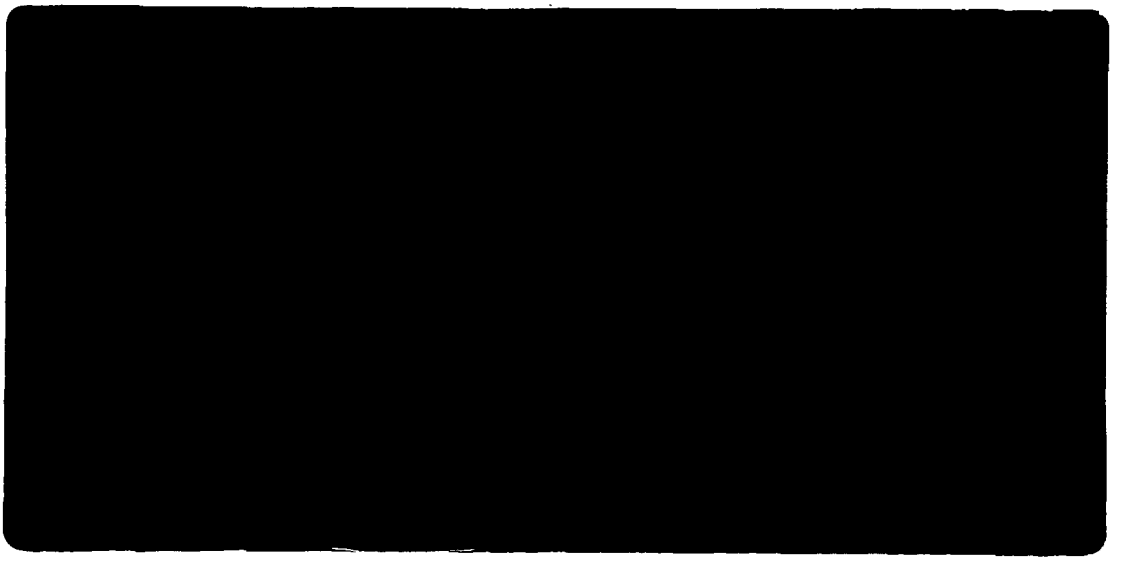

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Abstract

The environmental impact of a chemical is determined in part by its sorption properties. For the residual organic compounds generated in pulping and bleaching operations, sorption mechanisms will control their distribution between the sludge and wastewater discharge as well as their availability to participate in various chemical, physical and biological processes. In this presentation, the solids sorption of neutral organics from a water solution will be reviewed. The emphasis will be on general results from studies of organic sorption to an array of solid material including pulp-derived substrates.

Introduction

Pulping and bleaching processes inevitably lead to the production of a large array of residual organic species. Biological treatment of spent wash liquors only partially removes these compounds before the effluents are discharged into the environment (1,2). Although the fate of these chemicals is not well understood, it is believed that their ecological behavior correlates with their molecular weight and hydrophobicity. Of greatest environmental concern are the relatively small, neutral organic species such as chlorinated benzene derivatives which are known to be generated in chlorine bleaching processes. The relatively small size and low polarity of these compounds allows for their participation in hydrophobic transport mechanisms such as bioaccumulation (3-6).

The availability of these organic species to impact the environment is controlled in part by their distribution among the various phases of an effluent stream. An organic solute not affected by biological treatment will enter the environment as a freely solvated or solid-bound component of the sludge or wastewater discharge. Judging by the limited literature on the subject, little attention has been given to the distribution processes of hydrophobic organics in these systems. Fortunately, sorption processes of aqueous organics has been studied extensively with respect to other solid materials such as soil, sediment (7-12) and liquid chromatographic support materials (13-15). The purpose here will be the review of current knowledge on these other water/solid systems, including a discussion on research underway in our laboratories using pulp and pulp-derived solids.

Hydrophobicity

Water possesses a unique molecular structure which allows it to form a highly networked liquid state. This network tends to force out larger solutes which are unable to interact with water. The greater these repulsion forces, the more hydrophobic the compound is said to be. The hydrophobicity of a compound is typically gauged by its distribution between water and an organic phase, usually octanol. The octanol/water partition coefficient, K_{ow}, is defined as the ratio of the equilibrium concentration of a solute in the octanol phase to that in the water phase.

$$K_{ow} = C_o/C_w \qquad (1)$$

Because octanol is nonpolar and forms a relatively unstructured liquid, this distribution is believed mainly to be a result of the solute's interaction with water. Thus, a compound's K_{ow} value can be thought of as a direct measure of its aversion to water.

Hydrophobicity is often times the driving force that determines the environmental distribution behavior of a compound. For example, the transport of neutral organic species through the soil column is believed to be analogous to the movement of a water phase analyte through a nonpolar chromatographic column. The more hydrophobic the compound, the more time it will spend interacting with the solid phase. In the soil, this will affect the rate of transport, availability for biological degradation and the eventual fate of contaminants such as organic pesticides and other toxins released into the soil through spills or the leaching of solid waste material.

Most neutral organics including many of those found in the effluents generated from pulp and papermaking processes will have a log K_{ow} > 2 (Table 1) and demonstrate hydrophobic properties. It is likely that their ability to bind to solid material will affect not only their transport in effluent streams and transport and fate once released into the environment, but also their availability for biological treatment.

	Log K_{ow}
Chlorobenzene	2.84
1,2-Dichlorobenzene	3.38
1,3,5-Trichlorobenzene	4.02
1,2,4,5-Tetrachlorobenzene	5.05
Pentachlorobenzene	5.79
Benzoic Acid	2.03
Ethylbenzene	3.15
o-Chlorophenol	2.17
2,3-Dichlorophenol	3.15
2,4,6-Trichlorophenol	3.72
2,3,4,5-Tetrachlorophenol	5.03
Pentachlorophenol	5.06
3,4,5-Trichlorocatechol	3.75
Tetrachlorocatechol	4.23
3,4,5-Trichloroguaiacol	4.14
Tetrachloroguaiacol	4.60

Table 1. Log K_{ow} values for representative neutral organic species (ref. 15).

Equilibrium Sorption

The term sorption describes the process by which a chemical solute is transferred or distributed between two contacting phases. For water-solid systems, this could involve the sorption of an aqueous compound by one of many phases which makes up the solid. This point is important because the sorption behavior of a compound can be highly dependent on the nature of the substrate. In soil or

sediment particles for example, only about 5% of the mass is composed of organic species while the rest is composed of inorganic material, but it is the organic material which dominates the sorption of neutral organics. Although not proven, this appears to be a result of strong interactions between water and the soil or sediment particle's inorganic phases which prevents the interaction of hydrophobic organic species with these surfaces (16,17).

Experimentally, the equilibrium distribution of a solute between a water and solid phase is described in terms of its sorption isotherm. A sorption isotherm is the constant temperature relationship between the equilibrium concentration of a solute in the solid phase, C_s, to that in the water phase, C_w. Systems of environmental concern will typically demonstrate either linear or decreasing (nonlinear) isotherms (Fig. 1).

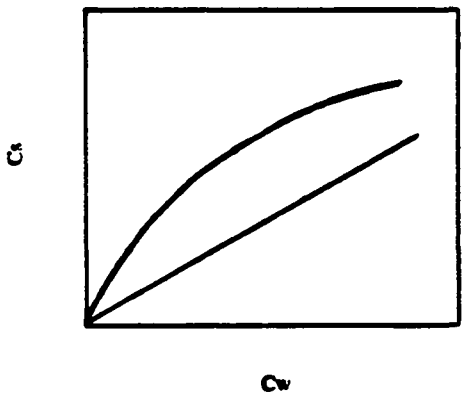

Figure 1. The sorption isotherm behavior for the water/solid sorption of neutral organic species.

In the case of a linear isotherm, results are reported in terms of a partition coefficient, K_p.

$$C_s = K_p C_w \qquad (2)$$

Decreasing isotherms are commonly fit with the Freundlich isotherm model which involves two fitting parameters, K_f and n.

$$C_s = K_f C_w^n \qquad (3)$$

For neutral organics distributing between water and solid phases at low loading, the isotherm is typically linear. Although the mechanism of distribution is poorly understood in these systems, the linear isotherm is often taken as evidence of solute absorption rather than a surface interaction (9,18,19). Octanol/water partitioning discussed earlier is a specific example of a absorption process. In this case, the neutral organic compounds are partitioning between water and an unstructured, liquid octanol phase which results in K_{ow} being a measure of how much "at ease" a compound is in water. For the partitioning of a neutral organic between water and a solid organic phase, this same argument is often applied, and has resulted in equations which relate partitioning of a neutral organic between water and a solid phase to its octanol/water partition coefficient.

These equations take the form of fitted log-log relations and can be found for various solids including soil, sediment, and biophases (8, 20-22). The log-log relation between the organic partitioning in soil or sediment samples, K_{oc}, and the octanol/water partition coefficient for a specific compound is maintained over a broad range of soil samples.

$$\log K_{ow} = a \log K_{oc} + b \qquad (4)$$

This indicates that the relatively minor variances in the organic makeup of these samples has little affect on the strong hydrophobic forces acting on the compound. Equations of this type are accurate over a broad range of neutral organic species. Outliers may include strongly polar compounds where other attractive forces lead to increased sorption, or compounds of high molecular weight where size may inhibit the partitioning process.

Sorption Kinetics

Hydrophobic sorption of an neutral organic by a solid particle involves the diffusion of the chemical from the bulk solution to the sorbent surface, the movement of the solute into the particle to locate an acceptable sorption site (in multiphase solids) and its attachment onto or partitioning into that site. The uncertainty in this mechanism makes the characterization of the sorption kinetics difficult. Empirically, the sorption of hydrophobic organics to soil, sediment and other solid materials show an odd fast-slow behavior. Starting out rapid, reaching 30 to 60% of equilibrium in a few minutes, and achieving final equilibrium only after a few days, weeks even months (23-25). This movement towards equilibrium is asymptotic in nature, with the rate becoming smaller with each time increment. The desorption process is not as well characterized, but it appears to be slow and difficult; becoming more so with increasing incubation periods of the equilibrated sorption system. Some studies have concluded that a percentage of the sorbed solutes are not recoverable (i.e., irreversibly sorbed) (26,27). This is not likely, but the concept of two solute components, one that is reversibly sorbed and one that is irreversibly sorbed on the time scale of interest, is a popular assumption in the development of empirical models (28).

An approach often used with limited success in describing the sorption mechanism of organics in water-solid systems assumes the diffusion of solute into the solid particles (i.e., pore diffusion) to be the rate limiting step of the sorption process (28-31). Here, the solute is quickly sorbed to the outside of the solid particle, but then must maneuver its way through the inner pore structure of the solid to find an acceptable sorption site where it promptly adsorbs or partitions within. In terms of this model, the observed fast-slow sorption is explained as the rapid sorption of solute to easily accessible locations followed by the slow diffusion and sorption to less accessible locations. The irreversibility effect is thought to be caused by the difficulty associated with movement out of a complex pore network; there are numerous pathways in, but only one way out. Although the application of this model has been successful in empirically describing the rate of sorption, it fails to accurately predict a phenomenon known as the solids effect (32).

The solids effect is the observed drop in partitioning of a compound with increased solids concentration (33-35). It is analogous to an equilibrium constant of a chemical reaction having a dependence on

one of the reactants. The effect is not detectable at low solids, but at higher solids loading the effect is quite dramatic. For example, the partitioning of 2,3,4,5,6,2',5'-heptachlorobiphenyl (a PCB compound) between water and sediment samples shows no solids dependence below 1,000 mg/L, but demonstrates an order of magnitude drop in the partition coefficient between 1,000 mg/L and 10,000 mg/L (Fig. 2). The effect becomes important in the modeling of chemical transport and fate of compounds in systems which involve a relatively high suspended solids level including lake sediments, infiltration water in soil columns and possibly suspended pulp-solids in the effluent streams of a paper mill.

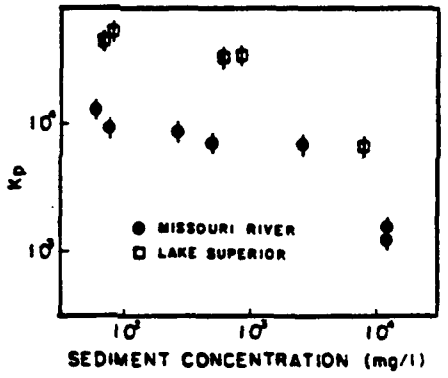

Figure 2. The solids effect on the sorption of aqueous 2,3,4,5,6,2',5'-heptaclorobiphenyl by sediment (ref. 11).

Currently, there is no universally accepted explanation for the solids effect. It appears to be a result of particle-particle collisions among the solids material (36-38). The frequency of these collisions will increase at higher solids levels and result in a steady-state balance between the sorbing compound and their collision induced desorption. We have proposed further research for the development and confirmation of this model because of its universal importance to the understanding of solute sorption in water/solid systems.

Sorption to Pulp-Derived Solids

The sorption of neutral organics by pulp has been the topic of two recent studies. Garbarini and Lion looked at the sorption of toluene and trichloroethylene to lignin and cellulose particles. They observed distribution coefficients of 120-150 for lignin-water partitioning and only 0-2 for the cellulose-water system (39). Daube et. al. found a distribution coefficient for the partitioning of aqueous dibenzodioxin into 40 kappa pulp and fully bleached fibers of 200 and 40, respectfully. These studies suggest that the primary sorbent in pulp is the lignin (40). This is similar to the sorption in soil and sediment solids where neutral organic sorption correlates to the organic fraction of the solids, except in pulp, the components of the organic phase appear to be distinct enough that their sorption behavior is separable.

In preliminary studies in our laboratory, the sorption of aqueous o-chlorophenol to fibers and fines of kappa numbers 26 and 0.3 also demonstrated a preference for the lignin phase. It also appears that sorption of o-chlorophenol by fines is greater than that by fibers. This may just be a surface area affect, but it may also be that the refining process (Valley Beater) used to generate the fines opens up the structure of the fibers making more of the lignin available to participate in the sorption process. Future work will attempt to better characterize the relation between sorption and kappa number. Studies are also planned to characterize sorption kinetics, and look at the sorption to actual water treatment solids.

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